

# SCIENCE FOR CERAMIC PRODUCTION

UDC 666.3:539.219.3:62-492.2

## EVALUATION OF THE DIFFUSION RATE IN SOLID-PHASE REACTIONS OF HIGHLY DISPERSE OXIDES

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The difference in the diffusion coefficients in complex oxide cations during synthesis results in the formation of a solid solution of the oxide containing the cation with the lower diffusion coefficient in the complex oxide, and also the phase consisting of the oxide with the higher diffusion coefficient or enriched by this oxide. Using highly disperse powders, it is possible to identify the cation which is the most mobile in synthesis, based on the oxide remaining in the product. This is demonstrated on the example of lanthanum chromite synthesis using the sol-gel method. An account of the variation in the relationship between the diffusion rates of lanthanum and chromium cations depending on the synthesis temperature and the polyvinyl alcohol in the gel is provided.

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Complex oxides (silicates, aluminates, chromites, ferrites, titanates, zirconates, etc.) are widely used in ceramic, glass, and binder technologies. Complex oxides are usually synthesized from simple oxides or compounds which in heat treatment convert to oxides. The diffusion rates of the cations which comprise a complex oxide are usually different, which leads to several effects. Let the diffusion coefficient of the cations  $K_1$  in a binary complex oxide be larger than that of the cations  $K_2$ . As the complex oxide is synthesized from simple oxides, the reaction front is shifted toward the crystal of the oxide containing  $K_1$  (the Kirkendall effect), and pores are formed within the same crystal (the Frenkel effect). Moreover, it brings about  $\gamma$ -nonstoichiometry in the complex oxide. As a rule, a solid solution of the oxide containing the cation with the lower diffusion coefficient ( $K_2$ ) in the complex oxide is formed, as well as a phase consisting of the oxide containing the cation with the higher diffusion coefficient ( $K_1$ ) or enriched with this oxide [1]. The presence of the second phase and the solid solution concentration have impact on all processes and ceramic properties sensitive to them: sintering, electrophysical characteristics, high-temperature creep, etc.

A deviation from stoichiometry in the complex oxide depends on the degree of nonequilibrium of its synthesis, and the higher this degree, the greater the difference of the syn-

thesized solid solution composition from the stoichiometric complex oxide [1]. This makes it possible to obtain solid solutions with a higher content of the oxide containing the cation  $K_2$ , as compared to the conditions approaching the equilibrium. Such solid solutions, due to their nonequilibrium, disintegrate when held at high temperatures. However, if ceramics are produced by hot pressing and operated at lower temperatures, it opens up possibilities for getting materials with unusual properties.

A high degree of process nonequilibrium is ensured when highly disperse simple oxide powders are used in the synthesis. Under these conditions, the oxide containing  $K_1$  cation is present in excess and can be easily identified. This fact can be used to identify the cation which has the higher diffusion rate in the course of synthesis. This information is essential for the development of ceramic technologies, in particular, synthesis and sintering technologies. The purpose of the present paper is to show the possibility of using this method to identify the cation which has a higher diffusion rate and the conjectured reactions of defect formation in synthesis.

To illustrate this approach, we use the data from [2]. The authors investigated the synthesis of lanthanum chromite using the sol-gel method. Aqueous solutions of lanthanum and chromium nitrates were distributed in polyvinyl alcohol (PVA) gel and heat-treated, which ensured the high dispersion of the simple oxide powders and, accordingly, a high degree of nonequilibrium of the lanthanum chromite synthesis.

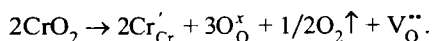
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The initial mixtures were taken in the stoichiometric ratio for the synthesis of  $\text{LaCrO}_3$ . The authors varied the PVA content and the synthesis temperature and determined the phase composition of the end product using the x-ray phase analysis. The process of synthesis was analyzed on a derivatograph as well.

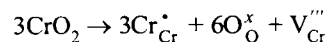
Synthesis at a temperature of  $700^\circ\text{C}$  revealed that  $\text{La}_2\text{O}_3$  is present in excess. This is the evidence of the fact that the lanthanum cation under these conditions diffuses faster than the chromium cation. However, at higher temperatures ( $800$  and  $900^\circ\text{C}$ ) the situation changes.  $\text{Cr}_2\text{O}_3$  begins to be in excess, i.e., the chromium cation under these conditions exhibits a higher diffusion rate than the lanthanum cation.

The variation in the oxidation level of the chromium cations has the deciding and most significant effect in the synthesis of  $\text{LaCrO}_3$ . At low temperatures, the synthesis process occurs via the chromium compounds at a higher oxidation level than  $3+$  [2]. It can be  $\text{Cr}^{6+}$  or  $\text{Cr}^{4+}$  [2]. To account for these results, let us assume for simplicity that the oxidation level is  $4+$ . As the oxidation level increases, the chromium diffusion rate ought to decrease. Therefore, the synthesis of  $\text{LaCrO}_3$  at a temperature of  $700^\circ\text{C}$  is accompanied by the faster diffusion of lanthanum cations than that of chromium cations, and  $\text{La}_2\text{O}_3$  is present in excess. The transition of the chromium to a lower oxidation level ( $3+$ ) apparently occurs at temperatures of  $700 - 750^\circ\text{C}$ , which is testified by the acceleration in the mass loss registered in the thermogram and the peak in the DTG. The diffusion of the chromium cations, on the contrary, is additionally retarded by the fact that as the oxidation level decreases, which has to be accompanied by oxygen volatilization, oxygen vacancies which retard the mass transfer are formed in the chromium oxide (by convention,  $\text{CrO}_2$ ):

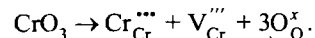


Due to the oxygen loss at temperatures of  $680 - 750^\circ\text{C}$ , the chromium at the oxidation level of  $4+$  (or  $6+$ ) in the chromium sublattice is replaced by  $\text{Cr}^{3+}$ . The relationship between the diffusion rates of lanthanum and chromium in this case is reversed. The rate of this change in the situation, namely, the oxygen volatilization and the transition to the  $\text{Cr}^{3+}$  cation sublattice, depends on the surface area of contact with the gas medium, i.e., on the specific surface area of the powder. The specific surface area of the synthesized powders increases with increasing PVA content in the mixture [2]. It can be assumed that the specific surface areas of the lanthanum and chromium oxides formed in the intermediate stages of synthesis increase as well. After the main part of the chromium passes to the oxidation level of  $3+$ , the remaining  $\text{Cr}^{4+}$  (and, possibly,  $\text{Cr}^{6+}$ ) act as additives. By replacing  $\text{Cr}^{3+}$ , they cause the formation of chromium cation vacancies, which facilitates the acceleration of its diffusion. The fastest diffusing cation in these conditions is chromium and

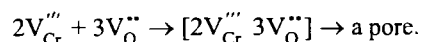
not lanthanum, which results in the presence of chromium oxide in the product:



or



The system dissipates its excess energy through pore formation due to the decrease in the concentration of oxygen and cation vacancies:



However, this process takes time. The larger the interface (the higher the PVA content), the faster the process of oxygen volatilization and transition to the sublattice  $\text{Cr}^{3+}$  in the chromium oxide, and the greater the nonequilibrium of this process. The residual  $\text{Cr}^{4+}$  and  $\text{Cr}^{6+}$  act as additives and lead to the chromium cation vacancies in the  $\text{Cr}^{3+}$  sublattice. As a consequence of the high concentration of oxygen vacancies due to the oxygen volatilization, a great number of vacancies of both signs, which do not have time to merge into pores, remain within the system. This ensures a higher rate of chromium cation mass transfer, as compared to the lanthanum cations, and free chromium oxide remains in the system after the synthesis. A decrease in the interface surface (the PVA content) produces a decrease in the degree of nonequilibrium of the process. The system in these conditions has time to reduce the number of vacancies in the chromium oxide through their merging in pores. The rate of chromium cation mass transfer is retarded and approaches the mass transfer rate of the lanthanum cations. This is precisely the case, when neither  $\text{La}_2\text{O}_3$  nor  $\text{Cr}_2\text{O}_3$  were identified in the lanthanum chromite synthesis product [2].

Thus, in the synthesis of complex oxides from high-dispersion powders, the analysis of the end products makes it possible to identify the cation which has the higher diffusion rate in synthesis, judging from the residual free oxide. Based on the defect formation reactions, it is possible to put forward a hypothesis for the mechanism of synthesis. In order to obtain a complex oxide with a near-stoichiometric composition, it is necessary to lower the degree of nonequilibrium of the synthesis process and thus to allow time for the system to complete the synthesis. This can be accomplished by different methods. Thus, in the synthesis of lanthanum chromite using the sol-gel method, approximation of the stoichiometric composition is accomplished by varying the PVA gel content in the initial mixture. The optimum value of the resulting specific surface area makes it possible to equalize the mass transfer rates of lanthanum and chromium cations and to prevent the presence of free oxide in the synthesized product.

In the synthesis of  $\text{MgCrO}_3$ , when samples consisting of the mixtures of simple oxides taken in the stoichiometric ratio were sintered, the difference in the sizes of the initial simple oxide powders was used to equalize the mass flows of the magnesium and chromium cations [3]. The chromium oxide particles had a smaller size than the magnesium oxide particles [3]. In this way the mass flow of the chromium cations was increased. In the synthesis of lanthanum chromite, the mass flows were equalized due to a certain decrease in the PVA content in the initial mixture. It is probable that in the sol-gel method, the mass transfer rate of chromium cations at synthesis temperatures above  $750^\circ\text{C}$  is higher than that of lanthanum cations and has to be somewhat decreased.

Analysis of the reaction products of the complex oxide synthesized from highly disperse simple oxide powders makes it possible to easily identify the cation whose mass transfer under the particular conditions of the synthesis is higher. This cation is part of the composition of the synthesized powder in the form of free oxide. The identification of

the cation whose mass transfer in synthesis is higher makes it possible to deliberately modify the synthesis conditions in upgrading the technology of ceramics made of complex oxides and predicting its properties. Moreover, it opens up possibilities for obtaining materials based on the nonequilibrium solid solutions, which may be promising as sensors and electronic materials.

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